Aeronautical Research Institute, University of Tokyo
Report No. 387 March 1964

Sintering and Some Properties of Iron-Bonded Titanium Carbides

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Summary. A study has been done on the iron-bonded titanium carbides. Mixtures of titanium carbide and iron powders in various compositions (10, 20, 30, 40, 50, 60 ,70, 80 and 90 pct iron by weight) were prepared. Linear shrinkage of compact was observed during sintering and optimum temperature for sintering was determined. Then test specimens were sintered and density, transverse rupture strength and hardeness were evaluated on the specimens in three different conditions ; as sintered, quenched and tempered. Though some properties of iron-bonded titanium carbides are inferior to nickel-bonded titanium carbides, the promising characterisrics of iron-bonded titanium carbides of higher binder content (60–80 pct iron) are that those have heat treatability by dissolution of free carbon in titanium carbide into binder phase.

1. INTRODUCTION

Considerable work has been carried out on various cermet systems during the past ten years. Of those systems, the TiC base cermets were considered to be most promising and the greater part of work has been made on the TiC-Ni or TiC-Co cermet systems. Little work, however, has been reported on the TiC-Fe cermet system, probably by lack of conditions to form cermet [*1*]; poor wettability between iron and titanium carbide [*2*], and low solubility of titanium carbide in liquid iron at high temperatures [*3*], [*4*].

Titanium carbide of commercial grade more or less includes free carbon. Supposing that the free carbon in titanium carbide dissolves into iron during the liquid-phase sintering, and the solubility of titanium carbide is extremely low, the binder phase will become carbon steel, provided that the proper amount of free carbon is included. Then the composite material combined the carbide and steel matrix would be comparatively soft in the annealed condition, but capable of being hardened by quenching, approaching to the properties of cemented carbide. For higher binder content, the material is pretty ductile and can be cut and machined by the conventional techniques. The characteristics of such a material are much interesting for several applications.

The study described in this paper was projected to investigate the conditions of sintering, some physical and mechanical properties, and capability of heat treatment of the TiC-Fe cermet system.

2. Experimental Procedure

The titanium carbide powder was of commercial grade and an average particle size was 6.5μ. According to chemical analysis, a combined carbon content was 18.50 pct and 0.35 pct free carbon. The iron powder used was reduced one and −325 mesh. Mixtures of powders in various compositions (10, 20, 30, 40, 50, 60, 70, 80 and 90 pct iron by weight) were ball milled for 25 hrs in methyl alcohol, and dried.

First, the optimum conditions of sintering were studied by measuring linear shrinkage of a compact during sintering with a photographic method. The equipment consisted of a sintering furnace and a photographic apparatus is schematically shown in Fig. 1. The photographic apparatus is consisted of a singlelens-reflex camera of conventional type, a long focus lens and an extension bellows. The linear shrinkage was evaluated by measuring the length of image on a film with an optical comparator. The reason why a photographic method was employed in the present study, instead of a more precise or a convenient automatic recording method, is that the change in shape of a compact during sintering can be observed at the same time as shown in Photo. 1, which is apt to occur in a compact of higher binder content as interested in this study. A preliminary work on a linear shrinkage measurement during sintering of TiC-Fe cermet system was read in 1962.* However, we found later that the same technique had been used for the similar purpose by other investigator [5].

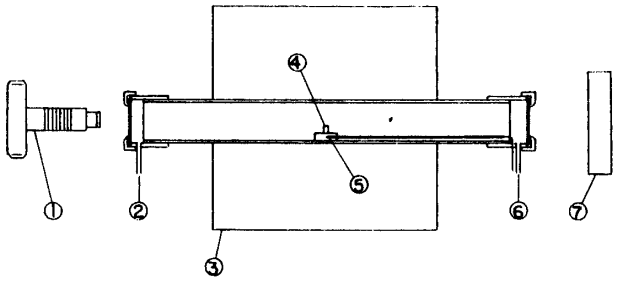

Figure 1. Schematic illustration of the apparatus for measuring shrinkage during sintering : (1) camera, (2) hydrogen inlet, (3) furnace with silicon carbide heating element, (4) specimen (5) thermocouple, (6) hydrogen outlet, (7) background lamp.

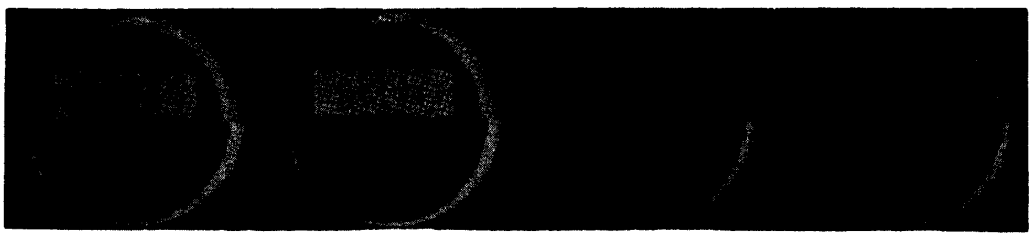

Photo. 1. Change in specimen shape during sintering.

*: read before the annual meeting of the Japan Institute of Metals held in April, 1962.

After measurement of linear shrinkage of compacts of various compositions, optimum temperatures for sintering of each composition were determined. Test specimens of various compositions were prepared by pressing at 2 t/cm^2 and sintered at the optimum temperature for each composition for 1 hr in a dry hydrogen atmosphere. Then transverse rupture strength and hardness were evaluated for three conditions; as sintered, quenched and tempered. Coefficient of thermal expansion was determined, and oxidation test was also performed.

3. Results and Discussion

Linear shrinkage curve of a compact of 70 pct iron is shown in Fig. 2. A compact of $6 \times 10 \times 30$ mm^3 was heated up to 1500°C at a rate of 300°C/hr in a dry hydro-

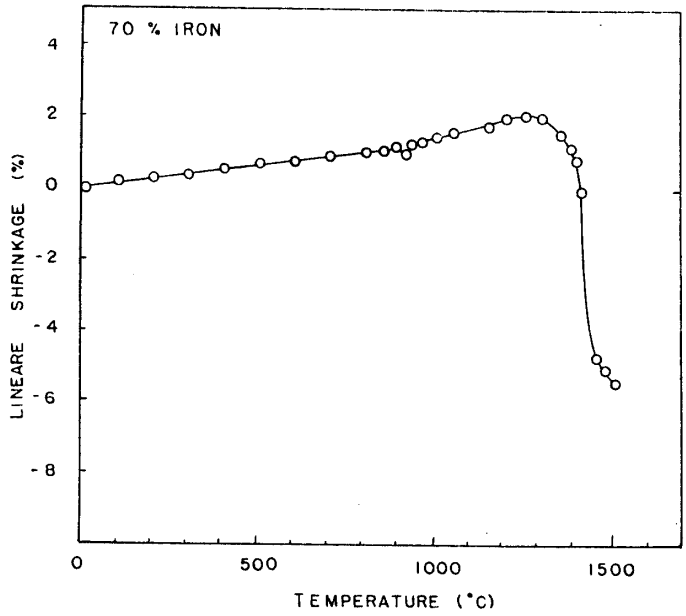

FIGURE 2. Shrinkage curve of a compact of 70 pct iron heated up to 1500°C at a rate of 300°C/hr

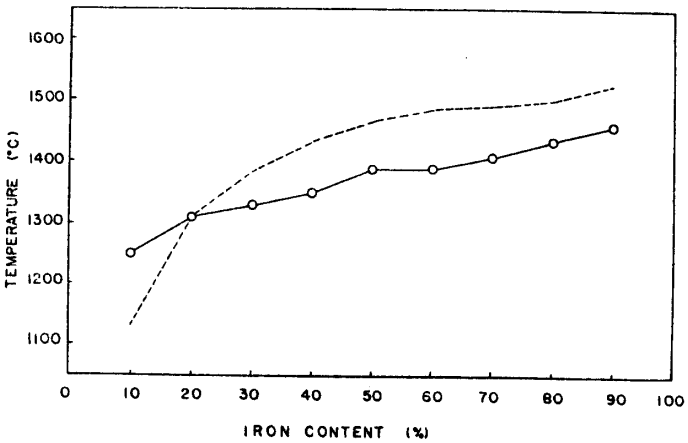

FIGURE 3. Temperature of the beginning of abrupt shrinkage in the shrinkage curve.

gen atmosphere. Compacts slightly expanded up to 1100–1300°C and then shrinking occured as shown in Fig. 1. The abrupt shrinkage was observed in the temperature range of 1250–1460°C depending on the composition. The temperature of beginning of the abrupt shrinkage, which presumably corresponds to the appearence of a liquid phase, is plotted against iron content in Fig. 3. The carbon content of binder phase was calculated as listed in Table 1, assuming that all the free carbon in titanium carbide dissolve into iron. If the mixture of two differnt kind of powders is heated to high temperature, diffusion will occur between particles and the trend of phase change will be estimated by the equilibrium in the phase diagram of the two substances [6], and thus the temperature at which a liquid phase appears on heating could be estimated. For the ternary system of C-Fe-Ti, however, detailed data for higher titanium and carbon region have not been reported. The differnces between experimental values and those determined by the aid of the

TABLE. 1. Composition, carbon content in binder phase, and sintering temperature.

Composition		Carbon in binder phase	Sintering temperature
Fe (%)	TiC (%)	(%)	(°C)
90	10	0.04	1475
80	20	0.09	1475
70	30	0.15	1470
60	40	0.23	1470
50	50	0.35	1470
40	60	0.52	1450
30	70	0.81	1425
20	80	1.38	1400
10	90	3.05	1400

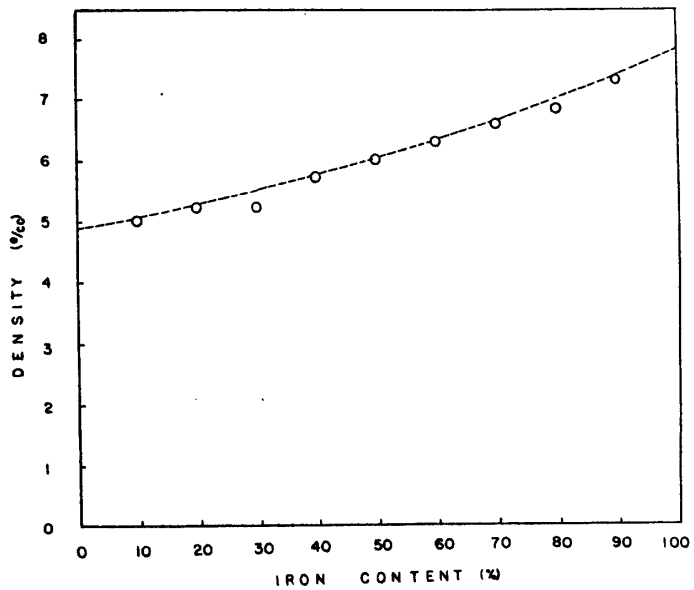

FIGURE 4. Apparent dencity as a function of composition. Dotted line shows calculated value.

phase diagram of binary C-Fe system (dotted line in Fig. 3) are considerably large as shown in Fig. 3. Therefore, the optimum temperatures for sintering were empirically determined after the testings of shrinkage, density and strength. The determined sintering temperatures are also listed in Table 1.

Test specimens were prepared by pressing mixed powders at 2 t/cm^2 and sintered at the temperatures listed in Table 1 for 1 hr in a dry hydrogen atmoshere. Specimens were ground after sintering with a diamond wheel and finisned to the size of $3\times8\times26\sim28$ mm^3. Transverse rupture strength was evaluated for three conditions of specimen ; as sintered, quenched and tempered. Quenching was carried out by heating specimens for 1 hr to the quenching temperatures for ordinary carbon steels of the same carbon content and then quenching into water.

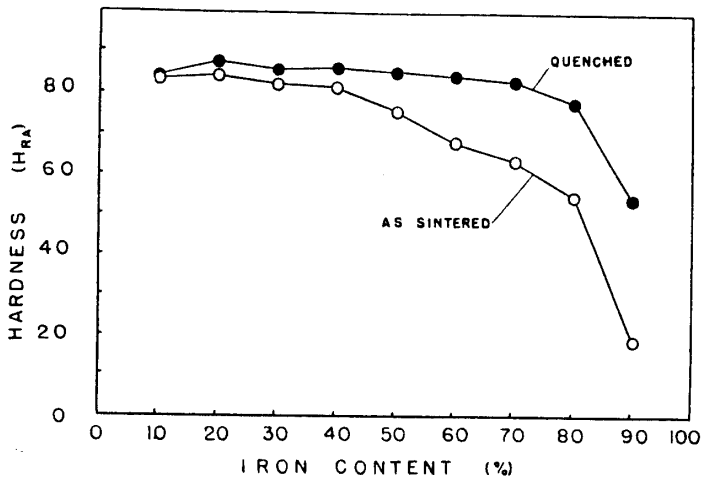

FIGURE 5. Hardness as a function of composition and the effect of quenching.

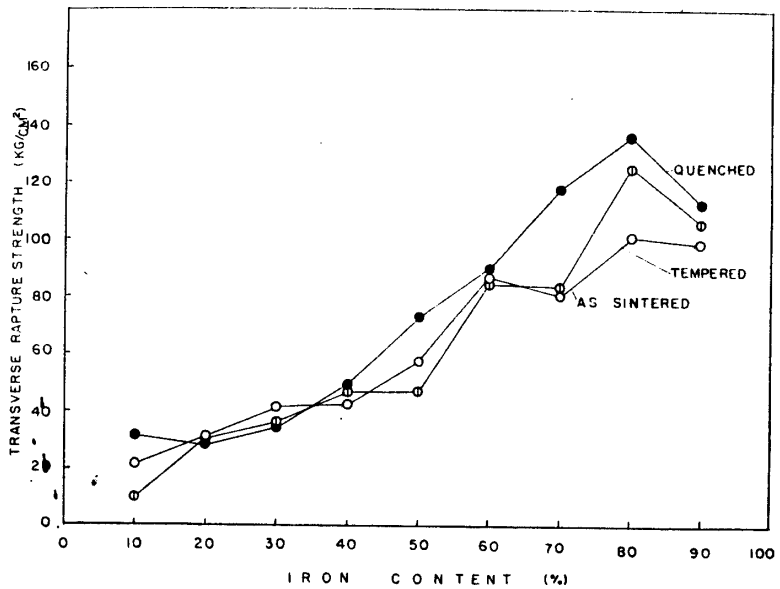

FIGURE 6. Transverse rupture strength as a function of composition and the effect of heat-treatment.

Tempering was carried out by heating specimens at 500°C for 1 hr. Density, hardness and transverse rupture stregth are plotted against composition in Figs. 4,

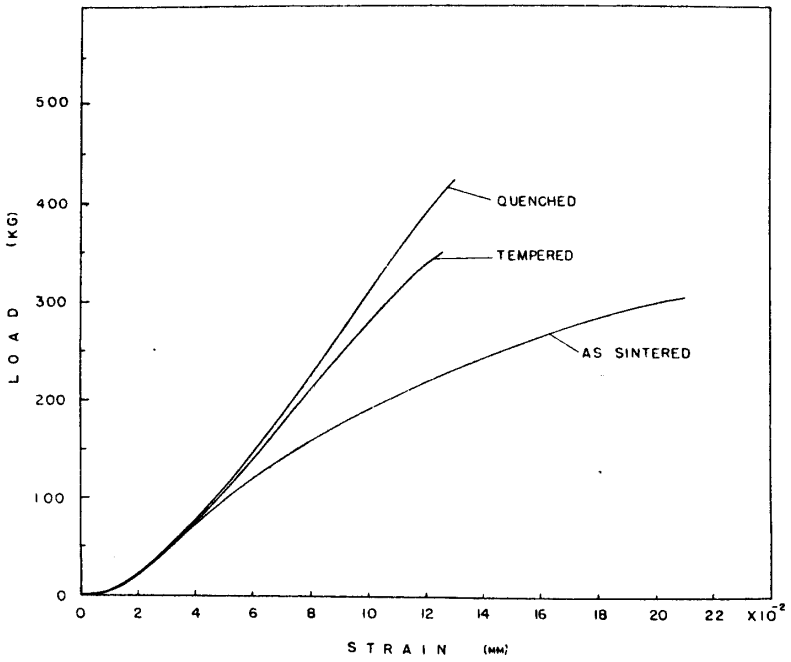

FIGURE 7. Change of load-strain curve in transverse rupture test affected by heat-treatment.

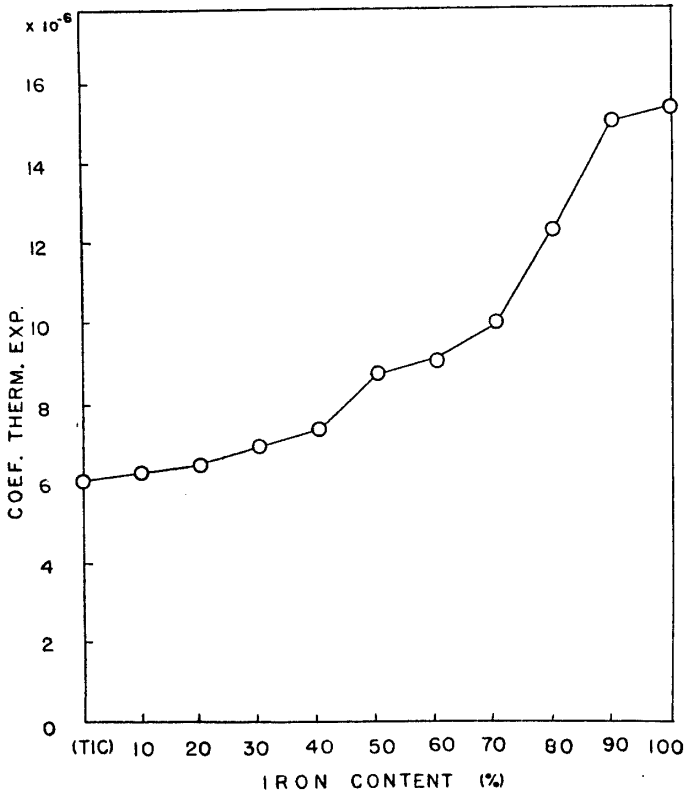

FIGURE. 8. Coefficient of linear thermal expansion as a function of composition.

5 and 6. Fig. 5 clearly shows that these materials can be hardened by quenching. Transverse rupture strength was tested by three point loading of 20 mm span. Fig. 6 shows that the effect of quenching is remarkable for the composions higher than 50 pct iron, but that of tempering is not invariably good. Fig. 7 shows the change in load-strain curve by heat-treatment, in which strain was evaluated by the deflection of a middle point of a specimen. Coefficient of linear thermal expansion was determined by an optical dilatometer and plotted against iron content in Fig. 8.

In the closest arrangement for a packing of unifom spheres, porosity is about 26 pct by volume [7]. Assuming that the uniform spheres of titanium carbide in the closest arrangement are completely cemented with iron, the weight ratio of titanium carbide to iron becomes 64 : 36. The particles of titanium carbide are not of uniform size and shape. Furthermore, titanium carbide dissolves into iron at higher temperatures. The ratio, however, would not deviate so much from the range of 20–40 pct iron by weight. Therfore, the binder phase will become continuous in the sintered body of the iron content higher than 40 pct, provided that the wettability between titanium carbide and iron is considerably good. The transverse rupture strength and coefficient of linear thermal expansion changed with iron content. In the former, the effect of heat-treatment is less remarkable for the compositions lower than 40 pct iron. On the other hand, the coefficient of linear thermal expansion gradually increases with iron content up to 40 pct iron, but large change occurs in the range higher than 50 pct iron. These changes with iron content can be explained fairly well by the above mentioned assumption that the continuity and the thickness of binder phase are changed with binder

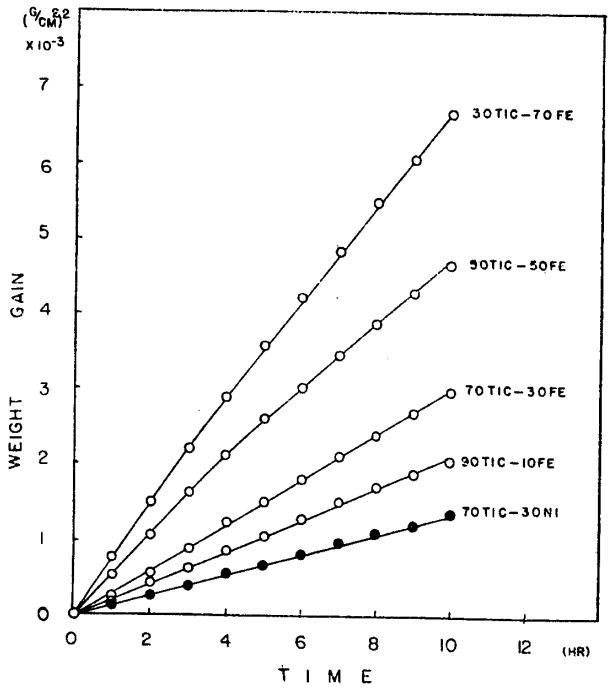

FIGURE. 9. Oxidation test conducted at 1100°C in air. Black circles represent nickel-bonded titanium carbide.

content.

Oxidation test was conducted by heating specimens at 1100°C in air. Compared with nickel-bonded titanium carbide, the oxidation resistance of iron-bonded titanium carbide is fairly inferior as shown in Fig. 9, as already reported [*8*]. Specimens of two of the highest iron contents were test cold-rolled. A specimen of 80 pct iron could be cold-rolled to 63 pct reduction without crack and of 90 pct iron was to 70 pct.

In order to make the composition of binder phase about the same the carbon content was adjusted to approximately 0.8 pct for the compositions of 40, 60 and 80 pct iron, and the similar tests were performed. The results were that the abrupt shrinkage occured at slightly lower temperatures in the composition of 80 pcti ron and apparent density increased a little in the compositions of 60 and 80 pct iron, but no significant changes were found on the other properties.

It has been reported that the addition of sulfur or iron-group sulfides improved the mechanical properties of sintered body of iron powder [*9*] [*10*]. The effect of sulfur addition was investigated with powder mixtures including about 0.3 pct sulfur to iron content and adjusted carbon content to 0.8 pct. The results obtained were the lowering of the tempereture of appearence of the liquid phase due to the melting of FeS formed, the slight increase of density and no significant change in mechanical properties of the final product.

As a conclusion, though the iron-bonded titanium carbides are inferior to nickel-bonded titanium carbides as already reported [*11*], the important property of iron-bonded titanium carbides is heat-tretability, that is, capability of combinining machinability and workability with hard material under proper conditions.

4. Conclusions

(1) Sintering and some properties of iron-bonded titanium carbides have been studied. The optimum sintering temperatures for various compositions were determined, and physical and mechanical properties were evaluated.

(2) Iron-bonded titanium carbides of higher iron content (higher than about 50 pct) have heat-treatability which is brought about by the dissolution of free carbon in titanium carbide into binder phase. Besides, these materials can be machined by the conventional methods when in the annealed condition.

(3) Adjustment of carbon content and addition of sulfur in compact resulted in higher density, but significant improvement in mechanical properties could not be observed in sintered body.

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